Appendix A-3
Hydrogen Technology, 1900–1945

In addition to the considerations of liquid hydrogen for rockets by Tsiolkovskiy, Goddard, and Oberth, other concurrent activities contributed to hydrogen technology. The largest and best known of these were the development and operation of the large dirigibles in Germany, Italy, Great Britain, and the United States from 1900 to 1937. Much has been written about these giants of the sky that need not be repeated here.[1] Thousands of passengers were carried safely in hydrogen-filled dirigibles, yet there were many accidents, which finally killed the giants. The most spectacular—and final—accident involved the *Hindenburg*, filled with 200 000 cubic meters of hydrogen, which burst into flames at Lakehurst, New Jersey, on 6 May 1937, killing 13 passengers and 22 members of its crew as well as one ground crewman.[2] When the ease with which hydrogen-air mixtures can be ignited is examined, the wonder is that there were not more accidents. For example, the Germans found in 1912–1913 that faint, finger-length flames of hydrogen-air mixtures could be produced merely by rubbing rubberized surfaces together, and the same fabric generated static electricity if torn. One modern safety manual points out that the minimum spark ignition energy to ignite a hydrogen-air mixture at atmospheric pressure is 0.000019 joule.[3] If that means nothing to you, the manual warns against certain actions that can generate static electricity to ignite hydrogen in test areas: combing the hair, wearing clothes made of nylon or other synthetics or wool, and allowing furred animals in the area. The legacy of dirigible operations, where millions of cubic meters of hydrogen were generated, stored, transferred, and flown, is not so much the safety procedures, but fears of using hydrogen that the accidents instilled in the minds of so many people.

One aspect of dirigible activity not so well known was attempts to use hydrogen as a fuel. Dirigibles had to vent buoyancy gas and Paul Haenlein obtained a U.S. patent in 1872 to use that otherwise wasted gas in the dirigible's engines. Haenlein, however, used coal gas and apparently did not get around to using hydrogen.[4] Using hydrogen in dirigible engines surfaced again after World War I in Italy, Great Britain, Germany, and the United States. In 1920, two British investigators estimated that dirigible range could be increased 20 percent by burning the hydrogen usually vented. They found that an engine could operate on hydrogen as an additive or on hydrogen alone, but in the latter case there was a tendency to knock.[5] Similar results were found elsewhere but the idea never gained widespread use. Experiments in Germany and the United States on using hydrogen in diesels met with some success in 1935, but by then the use of hydrogen in dirigibles was close to the end.[6]

In addition to dirigible developments, another great stimulus to the development of hydrogen technology during the first four decades of the twentieth century was scientific investigation. Unlike dirigible applications, which were centered on gaseous hydrogen, the scientific investigations that advanced hydrogen technology were primarily concerned with low temperature phenomena.

Hydrogen Technology from Science, 1900–1940

Progress in developing equipment for liquefying gases during the last decade of the nineteenth century was matched by equally impressive gains during the first decade of the twentieth. Carl von Linde's air liquefaction equipment, capable of liquefying 8 liters per hour, was exhibited in Paris in 1900 and purchased by the College of France.[7] In 1902, a process for separating oxygen from air, developed by Georges Claude, was in commercial operation in France. Two years later the British Oxygen Company exhibited a hydrogen liquefier, designed by James Dewar, at the Louisiana Purchase Exhibition in St. Louis. The National Bureau of Standards purchased it for $2400 for low-temperature thermometry.[8] By 1905, Linde liquefaction plants were operating in both Germany and France, and in 1907 the Linde Air Products Company began operations in the United States.

In 1906 interest in low temperature phenomena was stimulated when a German chemist, Walther Nernst, postulated the third law of thermodynamics—that the total and free energies become equal as absolute zero is approached. Heike Kamerlingh Onnes, founder of the cryogenic laboratory at Leyden in 1894, reached 4.2 K when he first liquefied helium in 1908. By evaporating helium, scientists were soon able to reach within one kelvin of absolute zero.

In 1924–1926, a new era began in theoretical physics—wave (quantum) mechanics. It was introduced by a 32-year-old scientist, Louis Victor de Broglie, in his doctoral thesis. He postulated a relationship between the velocity or momentum of electrons and wave lengths of radiation. His work stimulated many other physicists, and among those who carried the theoretical work further were Clinton Davisson, George Thomson, Erwin Schrodinger, and Weiner Heisenberg. All won Nobel prizes in physics for their contributions.

Heisenberg, a 24-year-old German physicist, believed that the theory should include only observable elements. His new wave mechanics theory expressed wave length frequencies and intensities of radiation emitted by the atoms in matrix mathematics. He used his theory to postulate in 1926 that the hydrogen molecule existed in two forms, which subsequently were called orthohydrogen and parahydrogen. Heisenberg's 1932 Nobel prize in physics was awarded "for the creation of quantum mechanics, the application of which has, among other things, led to the discovery of the allotropic forms of hydrogen."[9]

In orthohydrogen, the two hydrogen nuclei in the molecule spin in the same direction; in parahydrogen, the two nuclei spin in opposite directions. The two molecules have different physical properties but their chemical properties are the same.

In 1927 a British physicist, D. M. Dennison, used Heisenberg's postulate to make one of his own. Earlier observations of the specific heat of hydrogen had indicated an anomaly; the rotational specific heat decreased with time and temperature. Dennison

postulated that this was caused by the two kinds of hydrogen not being in equilibrium at the lower temperature. In 1928, William Giauque and Herrick L. Johnston at the University of California at Berkeley attempted to test Dennison's postulate by keeping a sample of hydrogen at a low temperature for six months, but the observed changes were so small that their experiment was inconclusive. The following year another team of investigators, K. F. Bonhoeffer and P. Harteck, used a catalyst to obtain equilibrium at low temperature and obtained almost pure parahydrogen. They showed the differences between orthohydrogen and parahydrogen in terms of specific heat and thermal conductivity of the gases.[10]

At room temperature and above, ordinary hydrogen is 75 percent orthohydrogen and 25 percent parahydrogen. At 77.4 K (temperature of liquid nitrogen used for cooling) the hydrogen mixture at equilibrium is 52 percent orthohydrogen and 48 percent parahydrogen. At the boiling point of liquid hydrogen, 20.3 K, the equilibrium composition is 99.8 percent parahydrogen.* When gaseous hydrogen is liquefied, it will slowly and spontaneously seek equilibrium, with orthohydrogen changing to parahydrogen. At 20.3 K, the conversion releases more heat (532 joules per gram) than is required to vaporize the liquid (453 joules per gram), so that liquefied normal hydrogen evaporates completely on conversion to parahydrogen—even in a perfectly insulated container—a situation Dewar did not foresee. The vaporization loss during the conversion at 20.3 K amounts to about 1 percent of the stored liquid hydrogen per hour, a loss much too high to be tolerated in practical applications.[11]

Another line of scientific investigation that led to new information about hydrogen and provided a powerful stimulus for developing liquid hydrogen technology began at the University of California at Berkeley with the research of Gilbert Lewis and William Giauque in testing the validity of the third law of thermodynamics. In 1926 Giauque devised a method for attaining very low temperatures by an adiabatic demagnetization technique. It was now possible to get within a few thousandths of a degree of absolute zero. At these temperatures, thermal motion of atoms almost ceases and Giauque was able to measure energy changes associated with the transition in the states of the atoms. In 1929, Giauque and an associate, Herrick L. Johnston, published the results of a discovery that set in motion a train of events leading to the discovery of heavy hydrogen in 1931. In studying the spectrum of oxygen, they found that in addition to atoms of atomic mass 16, there were others with masses of 17 and 18. The three types of oxygen atoms existed in the atmosphere in the proportions of 3150:1:5, respectively, and gave an average atomic mass for oxygen of 16.0035.[12] This startled physicists and chemists, for the whole scale of atomic mass was based on oxygen with an atomic mass of 16.0; now the base and all masses related to it had to be changed. Giauque was awarded the 1949 Nobel chemistry prize for this and other contributions to low temperature physics.

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*Sources differ as to the boiling point of liquid hydrogen at 1 atm with some quoting 20.3 K and others 20.4 K. Some of the confusion comes from the fact that liquid hydrogen can be "normal" hydrogen (75% ortho, 25% para), "equilibrium" hydrogen (21% ortho, 79% para) or parahydrogen (99.8% para). Two National Bureau of Standards authors, Richard B. Steward and Hans M. Roder, in chap. 11, "Properties of Normal and Para Hydrogen," in *Technology and Uses of Liquid Hydrogen*, ed. R. B. Scott, W. H. Denton, and C. M. Nichols (New York: Macmillan, 1964), p. 380, give the boiling point at 1 atm for normal hydrogen as 20.380 K and for parahydrogen, 20.268, citing the work of Woolley, Scott, and Brickwedde for the former and Roder, Diller, and Weber for the latter.

Prior to the Giauque-Johnston discovery, Francis Aston developed a highly accurate (1:20000) spectrographic measurement technique and investigated a number of elements, including hydrogen. He measured hydrogen's mass as 1.00778, based on an oxygen mass of 16.0, which compared well with chemical determinations of hydrogen's mass of 1.00777.[13] The Giauque-Johnston change in oxygen's mass meant a greater difference between the spectropic and chemical measurements of hydrogen's mass. In 1931, R. T. Birge and D. H. Menzel concluded this difference to be too great for experimental error and postulated that among the hydrogen atoms of atomic mass 1 must be some of atomic mass 2 in the proportion of about 1 in 4500.[14] This was an exciting challenge to physicists and chemists and the race began to determine whether the Birge-Menzel postulate was correct.

The winner of the race was Harold Urey, who had studied at the University of California and was influenced by the work of Lewis and Giauque. Urey first had to concentrate the isotope to identify it. He calculated that the difference in vapor pressures would provide the means for concentrating deuterium by distillation of solid hydrogen at the triple point. He postulated that the same differences in vapor pressure might also apply to the liquid state. He turned to the National Bureau of Standards where F. G. Brickwedde agreed to help. Brickwedde evaporated 4000 cubic centimeters of liquid hydrogen near the triple point, ending up with only one cubic centimeter. In the fall of 1931, Urey and his assistant, G. M. Murphey, placed Brickwedde's sample in a spectrograph and established the presence of deuterium, beyond all doubt.[15]

Urey won the 1934 Nobel chemistry prize for his achievement. Eight months after Urey's discovery, E. W. Washburn discovered that hydrogen and deuterium could be separated by electrolysis. When water is electrolyzed and hydrogen gas escapes, the residual water contains a greater proportion of deuterium oxide (heavy water). This discovery led Norway to undertake large-scale production of heavy water at a hydroelectric plant at Rjukan. Since heavy water is a good moderator for atomic reactors, the Allies raided the Norwegian plant during World War II to prevent Germany's obtaining a supply of the isotope. Deuterium can also be concentrated by a diffusion process.[16]

In 1935, the third hydrogen isotope, tritium, was prepared by Lord Rutherford, Marcus Oliphant, and Paul Harteck by bombardment of deuterophosphoric acid with fast deuterons.[17]

In summary, the scientific interest in low temperature phenomena provided a powerful driving force for advancing the technology of liquid hydrogen. The spontaneous conversion of orthohydrogen to parahydrogen, the release of enough heat in the conversion process to vaporize the liquid hydrogen, and the use of a catalyst to speed the conversion process were discoveries essential to later developments of technology for the storage and transportation of liquid hydrogen in quantity.

Rocket Experiments with Liquid Oxygen and Liquid Hydrogen, 1937–1940

The first to experiment with a low temperature liquefied gas in a rocket was Robert Goddard, who began using liquid oxygen in 1921. By 1923, Goddard had successfully operated a gasoline–liquid oxygen rocket, incorporating pumps for both, on a test

stand. Three years later, on 16 March 1926, Goddard launched the world's first liquid-fueled rocket at Auburn, Massachusetts.

The first to profit from Goddard's experience were the Germans during the 1930s. The German A-4 (V-2) using alcohol–liquid oxygen was the first practical application of a liquid-fueled rocket and the first to be mass produced. The V-2 established beyond all doubt the practicality of using a low temperature liquefied gas as a rocket propellant.

With all the German experience with gaseous hydrogen in dirigible operations, plus their experience with liquid oxygen for rockets, it was inevitable that they would consider liquid hydrogen for rockets. They did, but according to Wernher von Braun, the experience was brief and the results not very satisfactory.

In 1932, Walter Dornberger, a Germany army officer, organized a small rocket research station on the artillery proving grounds at Kummersdorf.[18] Among the engineers brought there were von Braun, Walter Riedel, and Walter Thiel. By 1936, the Kummersdorf group had the basic concept for the A series of rockets, and Dornberger started construction of a new rocket station at Peenemünde the same year. In April 1937, von Braun left Kummersdorf to become the technical director at the new station.[19] Thiel stayed at Kummersdorf and continued research on novel injection methods, more effective cooling, and higher combustion chamber pressures using alcohol–liquid oxygen as propellants for experimental rocket engines. Thiel also tried other propellant combinations including gasoline–liquid oxygen, methane–liquid oxygen, hydrazine–nitric acid, liquid hydrogen–liquid oxygen, and liquid hydrogen–liquid oxygen–fluorine mixtures. The experiments covered combustion characteristics, cooling, and general handling aspects of the fuels and oxidizers. The small rocket engine (less than 200 newtons, or 44 lb thrust) could be regeneratively cooled with one or both propellants or by water in a separate system. Von Braun observed an experiment with liquid hydrogen:

> As to Thiel's liquid hydrogen tests with this set-up, I remember seeing liquefied (outside) air dripping from the supercold liquid hydrogen line. In discussing liquid hydrogen's potential, Thiel fully endorsed Oberth's earlier optimism, but pointed out that tightness of plumbing connections was a critical problem and the ever-present explosion hazard caused by accumulation of leaked-out hydrogen gas in an unvented structural pocket would require extreme care in the design of a liquid hydrogen-powered rocket or rocket stage.[20]

Von Braun remembered the hydrogen experiments as occurring between 1937 and 1940. The exploratory work was not followed up as the Germans concentrated on developing rockets using alcohol–liquid oxygen.